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Real-space formulation of the electrostatic potential and total energy of solids

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Abstract

We develop expressions for the electrostatic potential and total energy of crystalline solids which are amenable to direct evaluation in real space. Unlike conventional reciprocal space formulations, no Fourier transforms or reciprocal lattice summations are required, and the formulation is well suited for large-scale, parallel computations. The need for reciprocal space expressions is eliminated by replacing long-range potentials by equivalent localized charge distributions and incorporating long-range interactions into boundary conditions on the unit cell. In so doing, a simplification of the conventional reciprocal space formalism is obtained. The equivalence of the real- and reciprocal space formalisms is demonstrated by direct comparison in self-consistent density-functional calculations.

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The evaluation of the electrostatic potential and total energy of crystalline solids has been an ongoing problem since the earliest days of solid state physics.¹⁻⁶ In *ab initio* density-functional^{7,8} calculations, the electrostatic component of the potential is typically written as a sum of ionic (or nuclear, in the all-electron context) and electronic (Hartree) terms. In an infinite crystal, however, each of these terms diverges and the sum is only conditionally convergent due to the long-range $1/r$ nature of the Coulomb interaction. Similarly, the electrostatic component of the total energy is a sum of electron-ion, electron-electron, and ion-ion terms, each of which diverges in an infinite crystal but combine to yield a finite total electrostatic energy per unit cell.

It has been appreciated for some time that the divergences and conditional convergence of such extended lattice summations can be eliminated by formulating the summations in terms of neutral densities that are well localized in real and/or reciprocal (Fourier) space.² In the conventional reciprocal space approach for *ab initio* calculations of crystalline solids,^{6,9} divergences are eliminated by adding neutralizing densities to otherwise divergent Coulomb terms in such a way that the effects of the added densities cancel in the final expressions. Remaining long-range interactions are then rendered short ranged by transforming to reciprocal space, where smooth periodic functions, of infinite extent in real space, are well localized. The resulting expressions for the electrostatic potential and total energy contain structure factors and/or Ewald sums, and require at least $O(N \log N)$ operations to evaluate, where N is the number of atoms in the unit cell. Furthermore, since the reciprocal space approach uses a Fourier basis, boundary conditions are necessarily periodic in all directions. And since the approach relies on Fourier transforms, it is difficult to implement efficiently on large-scale parallel computational architectures due to the need for extensive interprocessor communications.

The limitations of the reciprocal space approach have inspired much research on real-space and local-orbital based approaches¹⁰⁻²⁷ which allow for better scaling, a variety of boundary conditions, and eliminate the need for Fourier transforms. In order to treat long-range Coulomb interactions in crystals, these approaches also generally formulate otherwise divergent summations and integrals in terms of neutral densities. Alemany *et al.*¹¹ employ a uniform neutralizing density in a real-space formulation of the Hartree term. Ionic terms are, however, computed as in the conventional reciprocal space formalism, using Fourier transforms. Other real-space formulations have employed localized neutralizing densities to eliminate the need for reciprocal space transformations altogether. Kane²⁵ employs neutralizing Gaussian densities to construct a rapidly convergent expression for the crystal potential and finite total Coulomb energy in the context of a real-space Wannier function approach. The formulation of Bachelet *et al.*²⁶ employs Gaussian representations of local ionic densities to construct total densities and potentials and associated neutral terms amenable to evaluation in real space. Tsuchida and Tsukada²³ employ a combination of localized and uniform neutralizing densities to construct neutral terms optimized for evaluation in real space. Ordejón *et al.*²⁷ form neutral terms by expressing potentials and energies in terms of neutral pseudoatomic densities and differences of the crystal density from these. The formulation of Fattebert and Nardelli²⁰ employs neutralizing Gaussian densities and associated potentials, in the spirit of the classical Ewald method, to render long-range interactions short ranged.

Here, we develop expressions for the electrostatic potential and total energy of a crystalline solid which are amenable to direct evaluation in real space in $O(N)$ operations. The expression for the total energy so obtained is variational in the output density and quadratically convergent. We eliminate the need for reciprocal space transformations and/or neu-

tralizing analytic functions by replacing long-range potentials by the localized charge distributions which generate them, and incorporating long-range interactions into boundary conditions on the unit cell. In so doing, we obtain a simplification of the conventional reciprocal space formalism.

In the pseudopotential approximation,⁹ the Kohn-Sham equations of density functional theory^{7,8} are given by

$$-\frac{1}{2}\nabla^2\psi_i(\mathbf{x}) + V_{\text{eff}}\psi_i(\mathbf{x}) = \varepsilon_i\psi_i(\mathbf{x}), \quad (1)$$

$$V_{\text{eff}} = V_I^l + V_I^{nl} + V_H + V_{xc}, \quad (2)$$

$$V_I^l = \sum_a V_{I,a}(\mathbf{x}), \quad (3)$$

$$V_I^{nl}\psi_i = \sum_a \int d\mathbf{x}' V_{I,a}^{nl}(\mathbf{x}, \mathbf{x}')\psi_i(\mathbf{x}'), \quad (4)$$

$$V_H = - \int d\mathbf{x}' \frac{\rho_e(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}, \quad (5)$$

$$V_{xc} = V_{xc}(\mathbf{x}; \rho_e), \quad (6)$$

$$\rho_e = - \sum_i f_i \psi_i^*(\mathbf{x})\psi_i(\mathbf{x}), \quad (7)$$

where ψ_i and ε_i are the Kohn-Sham eigenfunctions and eigenvalues, $V_{I,a}$ and $V_{I,a}^{nl}$ are the local and nonlocal parts of the ionic pseudopotential of atom a , ρ_e is the electronic charge density, the integrals extend over all space, and the summations extend over all atoms a , and states i with occupations f_i . (Atomic units are used throughout.) For simplicity, we omit spin and crystal momentum indices and consider the case in which the external potential arises from the ions. The nonlocal part V_I^{nl} and exchange-correlation potential V_{xc} are determined by the choice of pseudopotentials and exchange-correlation functional, respectively. V_I^l is the Coulomb potential arising from the ions and V_H is that arising from the electrons (Hartree potential).

In an infinite crystal, V_I^l and V_H are divergent and the total Coulomb potential $V_C = V_I^l + V_H$ within the unit cell depends on ions and electrons far from the unit cell due to the long-range $1/r$ nature of the Coulomb interaction. The latter constitutes a particular problem for real-space formulations. Both difficulties may be overcome, however, by replacing the long-range ionic potentials by the short ranged charge densities which generate them, and incorporating long-range interactions into boundary conditions on the unit cell. By construction, the local ionic pseudopotentials $V_{I,a}$ of each atom a vary as $-Z_a/r$ (or rapidly approach this) outside their respective pseudopotential cutoff radii $r_{c,a}$; where Z_a is the effective ionic charge and r is the radial distance. They thus correspond, by Poisson's equation, to charge densities $\rho_{I,a}$ *strictly localized* within $r_{c,a}$ (or rapidly approaching this). The local ionic potentials, both inside and outside $r_{c,a}$, may thus be replaced by corresponding charge densities localized within $r_{c,a}$. Figure 1 shows a typical local ionic pseudopotential and corresponding ionic charge density. The total ionic charge density is then

$$\rho_I = \sum_a \rho_{I,a}(\mathbf{x}), \quad (8)$$

where the summation extends over all atoms in the crystal. Since the ionic densities are localized in real space, however, the summation in the unit cell is in fact finite and readily

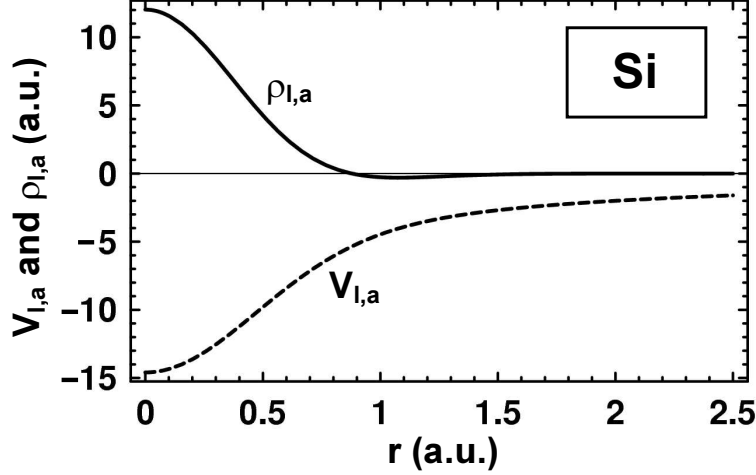


FIG. 1: Local part $V_{I,a}$ of Si pseudopotential²⁹ and corresponding localized charge density $\rho_{I,a}$. The potential has a long-range $1/r$ tail whereas the corresponding density is localized in real space. The total ionic density in the unit cell is thus readily summed in real space whereas the total ionic potential is not.

performed in real space, unlike the summation of ionic potentials. Having constructed the ionic charge density in the unit cell, the total charge density $\rho = \rho_I + \rho_e$ may then be constructed and the total Coulomb potential $V_C = V_I^l + V_H$ may be computed at once by a single Poisson solution subject to periodic boundary conditions:

$$\nabla^2 V_C(\mathbf{x}) = 4\pi\rho(\mathbf{x}); \quad (9)$$

whereupon V_{eff} may be evaluated as in (2).

The above formulation exploits the fact that, although long-range in real space, the $1/r$ nature of the ionic potentials outside r_c makes them physically equivalent to ionic densities localized within r_c ; and that, although depending physically on all ions and electrons in the crystal, the total Coulomb potential in the unit cell is determined completely by the total charge density within the cell, and the boundary conditions it must satisfy. In this sense, the contributions from all charges outside the cell are folded into the boundary conditions on the cell, as in the reciprocal space component of the classical Ewald formulation² and other more recent reciprocal³ and real¹⁴ space approaches. By computing the total Coulomb potential at once, individual divergences are eliminated. By formulating it in terms of localized functions within the unit cell, its evaluation can be accomplished in $O(N)$ operations, since the ionic charge at each point in the cell is contributed by a fixed number of neighboring atoms and the Poisson solution can be accomplished in $O(N)$ operations in real space by multilevel methods.¹⁵

In the pseudopotential approximation, the total energy in density-functional theory is given by

$$E_{tot} = T_s + E_{eI}^l + E_{eI}^{nl} + E_{ee} + E_{II} + E_{xc}, \quad (10)$$

$$T_s = \sum_i f_i \int d\mathbf{x} \psi_i^*(\mathbf{x}) \left(-\frac{1}{2}\nabla^2\right) \psi_i(\mathbf{x}), \quad (11)$$

$$E_{eI}^l = - \int d\mathbf{x} \rho_e(\mathbf{x}) V_I^l(\mathbf{x}), \quad (12)$$

$$E_{eI}^{nl} = \sum_i f_i \int d\mathbf{x} \psi_i^*(\mathbf{x}) V_I^{nl} \psi_i(\mathbf{x}), \quad (13)$$

$$E_{ee} = \frac{1}{2} \iint d\mathbf{x} d\mathbf{x}' \frac{\rho_e(\mathbf{x}) \rho_e(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}, \quad (14)$$

$$E_{II} = \frac{1}{2} \sum_{a, a' \neq a} \frac{Z_a Z_{a'}}{|\boldsymbol{\tau}_a - \boldsymbol{\tau}_{a'}|}, \quad (15)$$

$$E_{xc} = - \int d\mathbf{x} \rho_e(\mathbf{x}) \varepsilon_{xc}(\mathbf{x}; \rho_e), \quad (16)$$

where Z_a is the ionic charge of atom a at position $\boldsymbol{\tau}_a$ and, as in (1)–(7), the integrals extend over all space, and the summations extend over all atoms a and a' , and states i with occupations f_i . T_s is the kinetic energy of the non-interacting system; E_{eI}^l , E_{ee} , and E_{II} are the potential energies associated with the Coulomb interaction between electrons and ions, electrons and electrons, and ions and ions, respectively; E_{eI}^{nl} is the energy associated with the nonlocal part of the ionic potential; and E_{xc} is the exchange-correlation energy. T_s is determined by the Kohn-Sham orbitals and occupations, E_{eI}^{nl} is determined by the choice of pseudopotentials, and E_{xc} is determined by the choice of exchange-correlation functional.

In an infinite crystal, the total energy per unit cell may be obtained by restricting the integrals over \mathbf{x} and summation on a in (11)–(16) to the unit cell, while the integrals over \mathbf{x}' and summation on a' remain over all space. In this case, E_{eI}^l is divergent and negative while E_{ee} and E_{II} are divergent and positive due to the long-range $1/r$ nature of the Coulomb interaction. However, in terms of the total charge density ρ and Coulomb potential V_C , the finite total Coulomb energy per unit cell $E_C = E_{eI}^l + E_{ee} + E_{II}$ may be obtained at once:

$$E_C = -\frac{1}{2} \int_{\Omega} d\mathbf{x} \rho(\mathbf{x}) V_C(\mathbf{x}) - E_s, \quad (17)$$

where Ω is the unit cell and E_s is the ionic self-energy per unit cell. The ionic self-energy is subtracted so that E_C corresponds to the conventional density-functional Coulomb energy, which excludes ionic self-energy. This self energy may be computed from the ionic potentials and associated densities:

$$E_s = -\frac{1}{2} \sum_a \int d\mathbf{x} \rho_{I,a}(\mathbf{x}) V_{I,a}(\mathbf{x}), \quad (18)$$

where the summation is over atoms in the unit cell and the integrals are over all space. The integrals are readily evaluated as one dimensional radial integrals over a finite interval by virtue of the spherical symmetry and short range of the ionic densities. The remaining ion-ion energy in (17) corresponds to the point-ion energy (15) by virtue of the localization of the ionic charge densities within their respective pseudopotential cutoff radii: consistent with the frozen core approximation, there is negligible overlap.³³

The above formulation exploits the fact that, although the total Coulomb energy per unit cell depends physically on the contributions of ions and electrons throughout the crystal, it is determined completely, per unit cell, by the density and potential within the unit cell. Thus the need for reciprocal space transforms, structure factor computations, and/or Ewald sums is eliminated and the evaluation can be accomplished in $O(N)$ operations in real space.

In terms of the total Coulomb energy, the total energy per unit cell is then

$$E_{tot} = T_s + E_C + E_{eI}^{nl} + E_{xc}. \quad (19)$$

The orbital dependence in T_s and E_{eI}^{nl} can be eliminated in the usual way using the Kohn-Sham equations to obtain the relation

$$T_s - \int_{\Omega} d\mathbf{x} \rho_e(\mathbf{x}) V_{eff}^l(\mathbf{x}) + E_{eI}^{nl} = \sum_i f_i \varepsilon_i, \quad (20)$$

where V_{eff}^l is the local part of the effective potential which produces Kohn-Sham orbitals ψ_i and eigenvalues ε_i according to (1), and ρ_e is the electronic charge density corresponding to orbitals ψ_i according to (7). Combining (16)–(20), we arrive then at an explicit real-space expression for the total energy per unit cell in terms of the Kohn-Sham eigenvalues:

$$E_{tot} = \sum_i f_i \varepsilon_i + \int_{\Omega} d\mathbf{x} [\rho_e(\mathbf{x}) V_{eff}^l(\mathbf{x}) - \frac{1}{2} \rho(\mathbf{x}) V_C(\mathbf{x}) - \rho_e(\mathbf{x}) \varepsilon_{xc}(\mathbf{x}; \rho_e)] + \frac{1}{2} \sum_a \int d\mathbf{x} \rho_{I,a}(\mathbf{x}) V_{I,a}(\mathbf{x}). \quad (21)$$

In the self-consistent solution process, V_{eff}^l is the local part of the effective potential which produces Kohn-Sham orbitals ψ_i and eigenvalues ε_i . The electronic charge density ρ_e is constructed from the orbitals, the total charge density ρ is constructed from ρ_e , and the total Coulomb potential V_C , from ρ . With such accounting of self-consistent inputs and outputs, the input-density/potential dependence in the first term of (21) is exactly cancelled by the second, and the resulting expression is precisely equal to the Kohn-Sham functional (10) for a given input V_{eff} . It is thus variational in the output density ρ_e and quadratically convergent.^{9,28} Furthermore, it can be evaluated in $O(N)$ operations for a given Kohn-Sham spectrum and density.

To verify the equivalence of the present real-space formulation to the conventional reciprocal space formulation, we have implemented it in a finite-element electronic structure code²⁴ and compared eigenvalues and total energies to those produced by an established planewave code.^{30,31} Figure 2 shows the convergence of the total energy and lowest few eigenvalues produced by the real-space formulation to those produced by the reciprocal space formulation in a self-consistent crystalline GaAs calculation using the same pseudopotentials²⁹ and exchange-correlation functional.³² In this case, the reciprocal space results were converged to 10^{-9} Ha and so were taken as “exact” for the purposes of comparison. The real-space basis was then successively refined in a series of self-consistent calculations to allow analysis of the convergence of the real-space results to exact values. As the figure shows, both eigenvalues and total energy converge to the exact reciprocal space values over the full range explored, and do so at the optimal theoretical rate consistent with the cubic completeness of the real-space basis.

In summary, we have derived expressions for the electrostatic potential and total energy of crystalline solids which are amenable to direct evaluation in real space. Unlike conventional reciprocal space formulations, no Fourier transforms or reciprocal lattice sums are required, and the formulation is well suited for large-scale, parallel computations. The need for reciprocal space expressions is eliminated by replacing long-range potentials by equivalent localized charge distributions and incorporating long-range interactions into boundary conditions on the unit cell. In so doing, a simplification of the conventional reciprocal space formalism is obtained and the resulting expressions can be evaluated directly in real space in $O(N)$ operations.

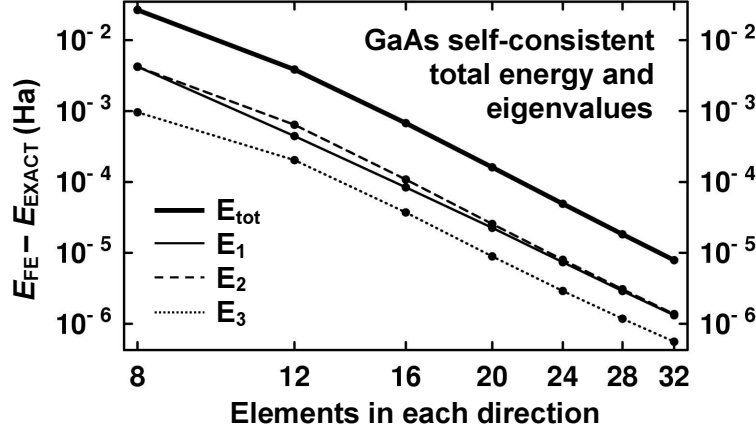


FIG. 2: Convergence of real-space total energy and eigenvalues to exact values in a self-consistent GaAs calculation. Here, “exact values” were obtained from a highly converged planewave calculation; and real-space values, from a series of finite-element calculations. The asymptotic slope of ~ -6 on the log-log scale shows that both total energy and eigenvalues converge to exact values at the optimal theoretical rate consistent with the cubic completeness of the finite-element basis: the error is $O(h^6)$, where h is the mesh spacing.

While the development here has been in the context of density-functional theory, and has been demonstrated by finite-element calculations, the ideas and/or expressions so obtained are applicable within a broad range of interaction models and basis sets.

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